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Fabrication and characterization of all-perovskite oxide p–n junctions based on $La_{1-x}Sr_xMnO_3$ and Nb-1wt% doped $SrTiO_3$

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Abstract

All-perovskite oxide p–n junctions have been fabricated by pulsed laser deposition. Semiconducting p-type $La_{1-x}Sr_xMnO_3$ (LSMO) and n-type Nb-1 wt% doped $SrTiO_3$ (NSTO) were used. Thin films of LSMO were epitaxially grown on (1 0 0) NSTO single crystal substrate at 650 °C and under an ambient oxygen pressure of 100 mTorr. Heteroepitaxial relationship of $(1\,0\,0)_{LSMO}||(1\,0\,0)_{NSTO}$ has been obtained. Good electrical rectifying characteristics have been observed at room temperature. LSMO is a well known colossal magnetoresistive material with a Curie temperature T_c at around room temperature. The *I–V* characteristics of the p-LSMO/n-NSTO junction were studied under the temperature range of 77–700 K and an applied magnetic field of up to 1 T.

Keywords: Films; Electrical properties; Transition metal oxides; p–n junction

1. Introduction

Perovskite oxides have attracted a lot of attention due to their diverse properties such as piezoelectricity, ferroelectricity, superconductivity, and magnetoresistance (MR) effect. Recently the fabrication of all-oxide p–n junction is one of the much sought-after research interests.[1–4] Due to the large bandgap thermal stability of oxide, it is believed that the operation of an all-oxide p–n junction will be stable even at temperatures up to several hundred degree Celsius; whereas common commercial diodes can function reliably at several tens of degree Celsius only. Indeed, the temperature dependence of the rectifying property of all-oxide p–n junction diode has been reported in several publications.[1,2]

Colossal magnetoresistance (CMR) effect has been observed in the family of manganese perovskite oxides.[5,6] $LaMnO_3$ is an antiferromagnetic insulator; however with the doping of divalent ions, p-type conducting oxide is formed. $La_{1-x}A_xMnO_3$ (A = Ca, Sr, Ba, etc.) has a phase transformation at the Curie temperature (T_c): ferromagnetic phase at low temperature ($T \leq T_c$), and paramagnetic phase at high temperature ($T \geq T_c$). In addition, it exhibits a strong negative MR effect. Recently manganite based p–n junctions have also been fabricated.[2–4] Sun et al. studied the magnetic field dependent rectifying characteristic of $La_{0.32}Pr_{0.35}Ca_{0.33}MnO_3$/Nb-$SrTiO_3$ junction.[4] They showed the band gap of $La_{0.32}Pr_{0.35}Ca_{0.33}MnO_3$ ($e_g\uparrow$–$e_g\downarrow$) varied with the magnetic state. The spin deviation of Mn^{4+} ions from fully ferromagnetic alignment caused a reduction of energy gap between e_g, and hence lowered the turn-on voltage of the junction.

We have fabricated all-oxide p–n junctions utilizing p-$La_{1-x}Sr_xMnO_3$ (LSMO) thin film grown on n-Nb-$SrTiO_3$ (NSTO) single crystal. In fact epitaxial LSMO thin film could be easily grown on NSTO by pulsed laser deposition (PLD). Two different compositions of LSMO thin films were studied: $La_{0.7}Sr_{0.3}MnO_3$ and $La_{0.85}Sr_{0.15}MnO_3$. $La_{0.7}Sr_{0.3}MnO_3$ is metallic-like at low temperature ($T \leq T_c$) and semi-conducting-like at high temperature ($T \geq T_c$).[2] With a well control of the deposition oxygen pressure, T_c of the films could be varied.[7] We prepared $La_{0.7}Sr_{0.3}MnO_3$ thin films at different deposition pressure from 60 to 150 mTorr, and checked their value of T_c carefully. In all subsequent p–n junctions fabrication, the deposition pressure was purposely adjusted for T_c to occur at around room temperature

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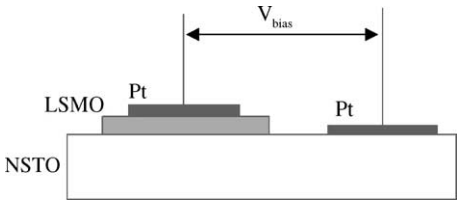

Fig. 1. Schematic side view of the LSMO/NSTO p–n junction.

and hence the effect of phase transition on the rectifying property could be investigated more easily. $La_{0.85}Sr_{0.15}MnO_3$ thin film was also grown as our p-layer. It has a completely different electric property compared with $La_{0.7}Sr_{0.3}MnO_3$. It is semi-conducting-like throughout the temperature range studied and the absolute resistivity is nearly six orders of magnitude larger than that of $La_{0.7}Sr_{0.3}MnO_3$. Two p–n junctions, namely $La_{0.7}Sr_{0.3}MnO_3$/NSTO and $La_{0.85}Sr_{0.15}MnO_3$/NSTO, have been fabricated. The influence of MR effect on the junction characteristics has been studied. We have also measured the current–voltage (*I–V*) characteristic at temperatures up to 700 K in order to evaluate the thermal stability of these junctions.

2. Experiment

The bulk $La_{0.7}Sr_{0.3}MnO_3$ and $La_{0.85}Sr_{0.15}MnO_3$ targets were fabricated by the standard solid state reaction of constituent oxides with the final sintering at 1320 °C in air for 10 h. Their structural properties and compositions were investigated by X-ray diffraction (XRD) and energy dispersive X-ray (EDX). LSMO films, having a spot area of 2.5×10^{-4} cm^2 as defined by the mask pattern, were grown on (1 0 0) NSTO single crystal substrate by PLD. A KrF excimer laser (λ = 248 nm) with a repetition rate of 10 Hz and laser fluence of ~5 J/cm^2 was used. The substrate to target distance was 4 cm. Before the deposition, the chamber was evacuated by rotary pump to approximately 1 mTorr. The deposition process was carried out under a substrate temperature of 650 °C and an ambient oxygen pressure of 100 mTorr for 10 min. Films with thickness of ~200 nm were formed. Post-annealing for 10 min at the same deposition atmosphere was carried out for all deposited oxide films to ensure good crystallinity. At last, Pt electrodes were grown on both the LSMO and NSTO. The schematic side view of these p–n junctions is shown in Fig. 1. We used XRD to characterize the structural properties of the LSMO films. The rectifying property of these junction diodes was measured at a temperature range of 77–700 K and under a 1 T magnetic field at room temperature.

3. Results and discussion

Fig. 2 shows the *I–V* characteristic of the two junctions Pt/LSMO and Pt/NSTO. Linear relationships traversing the origin indicate good ohmic contact in these junctions. Scanning probe microscope (SPM) image of the LSMO film suggests a surface roughness of only ~1 nm. Fig. 3a shows the θ–2θ XRD patterns of the PLD grown LSMO thin films on NSTO single crystal substrate. However, the lattice constant of LSMO (a = 3.89 Å) is so close to that of NSTO (a = 3.9 Å),

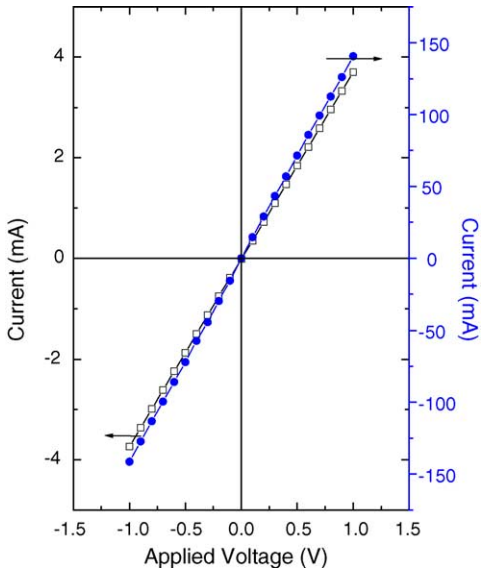

Fig. 2. Current–voltage characteristic curves of Pt/LSMO/Pt (□) and Pt/NSTO/Pt (●).

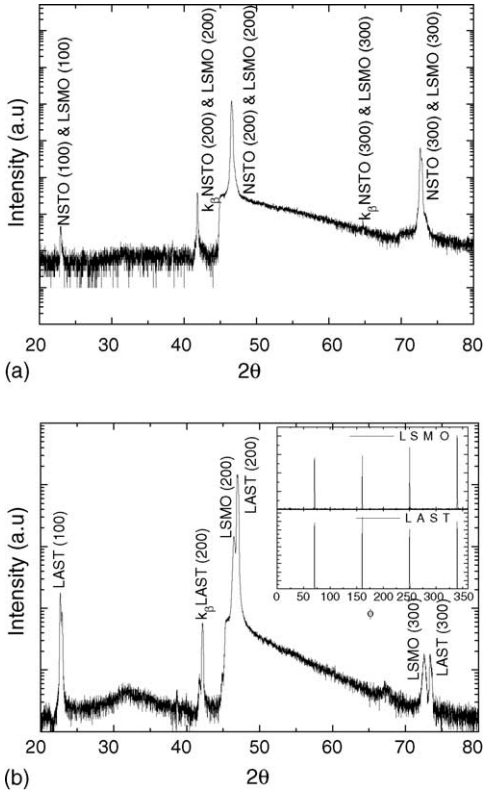

Fig. 3. X-ray diffraction patterns of LSMO films grown on (a) NSTO and (b) LAST.

diffraction peaks of LSMO and NSTO are completely overlapped. Nevertheless single phase of the film is evident in the XRD figure. In order to demonstrate good epitaxial relationship, however, an indirect method was used. We have grown LSMO on (La,Sr)(Al,Ta)O_3 single crystal substrate, which is cubic structure and has a lattice constant of 3.86 Å, at exactly the same deposition condition as those grown on NSTO. Fig. 3b shows that single phase LSMO has been obtained; and the epitaxial nature of the film is depicted in the inset of Fig. 3b, in which the four fold symmetry reflections of the film are seen to align with those of the substrate in the 360° ϕ-scan profile.

Attention has been placed on the selection of deposition condition of LSMO films, especially the ambient oxygen pressure. We have studied the effect of phase transition on the junction characteristic. It is known that the MR effect of manganese oxide is most prominent at around T_c. For ease of measurement, LSMO films with T_c at room temperature would be most desirable. We have grown single layer of LSMO films at different deposition pressure. $La_{0.7}Sr_{0.3}MnO_3$ appears to be more suitable for subsequent studies because of its well defined T_c and big change in electric transport property at around T_c. Fig. 4 presents the *R–T* profile of $La_{0.7}Sr_{0.3}MnO_3$ films deposited at different ambient pressure. All the three $La_{0.7}Sr_{0.3}MnO_3$ films show a clear transition from metallic-like at low temperature to semi-conducting-like at high temperature. Increase of deposition pressure raises the transition temperature, and the T_c value of the films gradually approaches to that of the bulk $La_{0.7}Sr_{0.3}MnO_3$. The data also reveals the oxygen dependence of the absolute resistivity of $La_{0.7}Sr_{0.3}MnO_3$. The resistivity of the

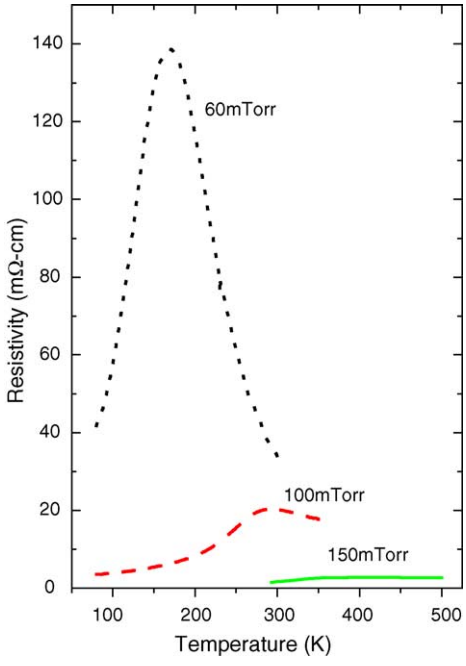

Fig. 4. Resistivity against temperature relations of LSMO films grown at different deposition oxygen pressure.

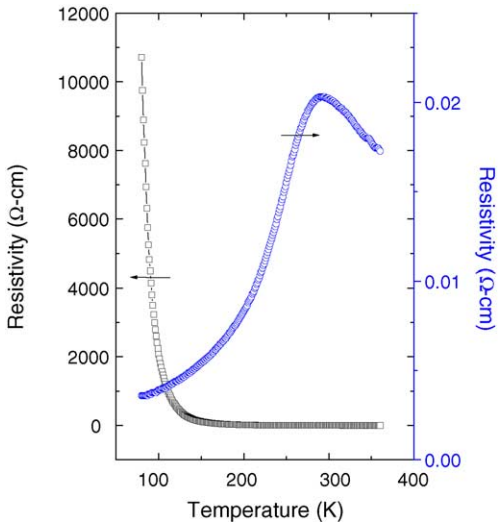

Fig. 5. Resistivity against temperature relations of LSMO films grown with different target compositions: $La_{0.7}Sr_{0.3}MnO_3$ (◯) and $La_{0.85}Sr_{0.15}MnO_3$ (□).

film grown at 60 mTorr is one order of magnitude higher than that of film grown at 100 mTorr. From these results, $La_{0.7}Sr_{0.3}MnO_3$ grown at 100 mTorr was selected because of the proximity of its T_c (290 K) to room temperature and its relatively low resistivity. At similar deposition conditions, $La_{0.85}Sr_{0.15}MnO_3$ film grown at 100 mTorr has also been fabricated. The resistivity of $La_{0.85}Sr_{0.15}MnO_3$ is six orders of magnitude higher than the resistivity of $La_{0.7}Sr_{0.3}MnO_3$. This is illustrated in Fig. 5. Two different p–n junctions using $La_{0.7}Sr_{0.3}MnO_3$ and $La_{0.85}Sr_{0.15}MnO_3$, respectively, have been fabricated at 100 mTorr. This is to investigate the effect of absolute resistivity on the junction characteristics. Room temperature *I–V* characteristic curves of the two junctions are displayed in Fig. 6. It shows that $La_{0.7}Sr_{0.3}MnO_3$ can form a better p–n junction with NSTO than $La_{0.85}Sr_{0.15}MnO_3$. The turn-on voltage of this junction is only 0.2 V. Indeed, the $La_{0.7}Sr_{0.3}MnO_3$/NSTO junction exhibits a good rectifying profile, showing a small leakage current and a large forward-based current. The influence of temperature on this junction over the temperature range between 77 and 700 K is shown in Fig. 7. The turn-on voltage of this junction decreases as the operation temperature is increased. It is 0.5 V at 77 K and 0 V at 700 K. The junction maintains an identifiable turn-on voltage till 380 K. At above 380 K a near ohmic relation is observed. Consequently with the operation temperature up to 600 K, a linear *I–V* curve is evident.

The MR effects of $La_{0.7}Sr_{0.3}MnO_3$ films at room temperature were measured. Although a high MR ratio at room temperature was expected. The MR ratio at the present LSMO films is only −4.5% under a magnetic field of 1 T. The *I–V* characteristic curve of our junction under a magnetic field of 1 T is plotted in Fig. 8. As mentioned by Sun et al.,[4] the application of magnetic field would modify the *I–V* relation significantly. In our studies, no noticeable difference in the *I–V* curve has been observed. The absence of discernable

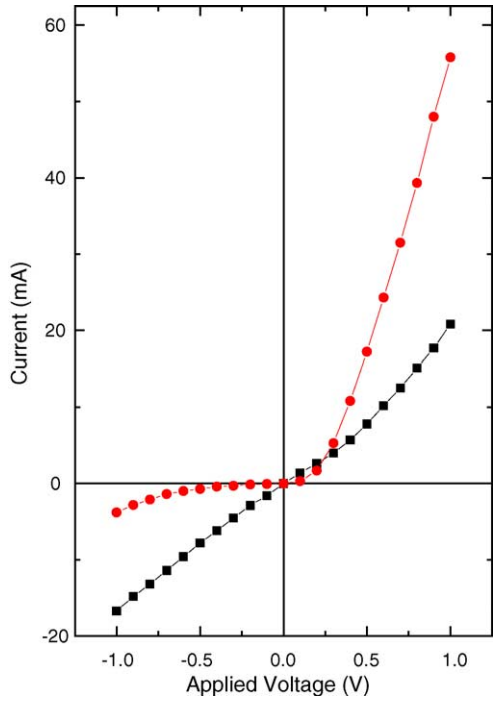

Fig. 6. Current–voltage characteristic curves of LSMO/NSTO p–n junction: $La_{0.7}Sr_{0.3}MnO_3$/NSTO (●) and $La_{0.85}Sr_{0.15}MnO_3$/NSTO (■).

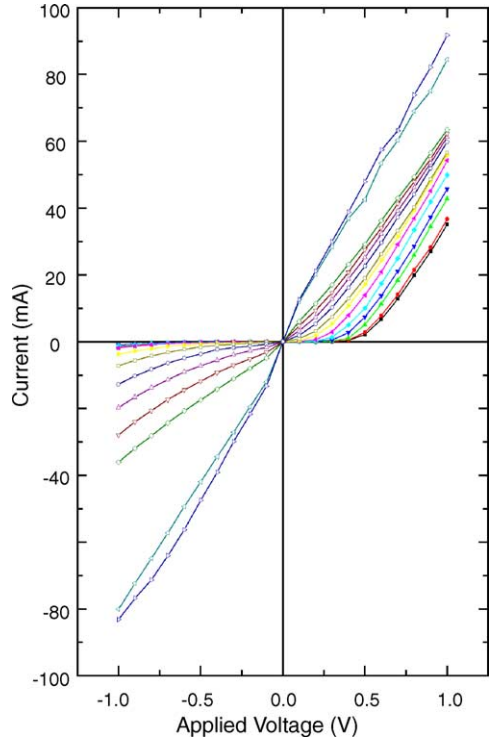

Fig. 7. Current–voltage characteristic curves of $La_{0.7}Sr_{0.3}MnO_3$/STON at different temperature: 77 K (■), 100 K (●), 140 K (▲), 180 K (▼), 220 K (♦), 260 K (◄), 300k (►), 340 K (□), 380 K (○), 420 K (Δ), 460 K (▽), 500 K (◊), 600 K (◁), and 700 K (▷).

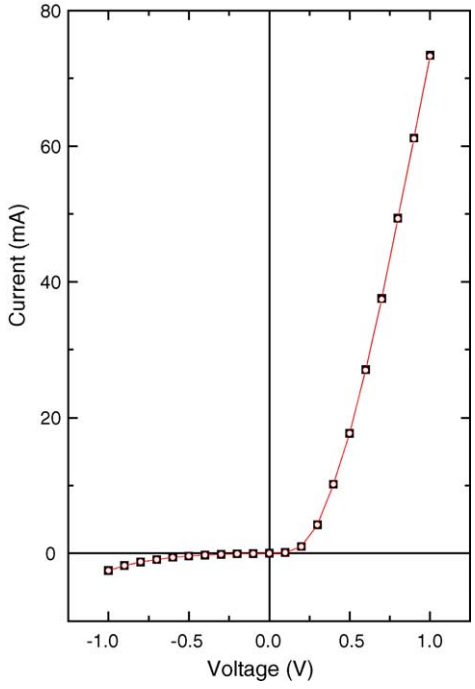

Fig. 8. Current–voltage characteristic curves of $La_{0.7}Sr_{0.3}MnO_3$/NSTO with (■) and without (○) the application of 1 T field.

effect in an external magnetic field may due to the small MR ratio of our manganite films (−4.5% as against the −90% reported by Sun et al.). The actual cause, however, needs further studies.

4. Conclusion

We have successfully fabricated an all-oxide p–n junction based on growing epitaxial p-LSMO layer on n-NSTO by PLD method. The $La_{0.7}Sr_{0.3}MnO_3$/NSTO shows good rectifying profile with a turn-on voltage of 0.2 V at room temperature. It maintains a junction rectifying property at the temperature up to 380 K. Although LSMO is a MR material, the junction is stable and shows no apparent different *I–V* characteristic under a magnetic field of up to 1 T.

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